The Adsorption of Gases at Low and Moderate Concentrations. Part I.—*Deduction of the Theoretical Adsorption Isostere and Isotherm.* Part II.—*Experimental Verification of the Form of the Theoretical Isosteres and Isotherms.*

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Part I.

In a previous paper* by the author it was pointed out that for small adsorptions the adsorption isotherm could be represented by the simple relation

$$\alpha = \alpha_0 c$$

where α is the amount absorbed and c is the equilibrium concentration outside the adsorbent. The present paper embodies an attempt to evaluate α_0 in the case of gases, and to connect it theoretically with other physical properties. In addition an adsorption formula is developed which applies to gases up to moderate adsorptions, that is up to 30 per cent. of the saturation value.

We will first examine the case of a gas at low concentrations. We will assume that upon the surface of the adsorbent there is a certain volume, determined, presumably, by the range of molecular action, which is occupied by the adsorbate. Then, for the change of energy involved in the adsorption at constant temperature of 1 grm. molecule of the gas by an infinite amount of adsorbent we can write down *three* expressions. The first of these is that obtained from thermodynamical reasoning by the author,† and we write the change of energy‡ as

$$\mathrm{E} = \mathrm{V}\left\{\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\boldsymbol{a}} - p\right\} = \mathrm{RT}^2\frac{\partial p}{p\partial \mathrm{T}} - \mathrm{RT} = \mathrm{RT}^2\left(\frac{\partial \log c}{\partial \mathrm{T}}\right)_{\boldsymbol{a}}, \tag{1}$$

where $p\mathrm{V} = \mathrm{RT}$ and $p = c\mathrm{RT}$.

A second and well-known expression may be obtained from the kinetic theory of gases§ and may be written

$$\mathrm{E} = \mathrm{RT}\log \mathrm{V}/\mathrm{V}_{\boldsymbol{a}}$$

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* ‘Roy. Soc. Proc. Edin.,’ vol. 39, p. 48 (1919).

† *Ibid.*, vol. 38, p. 23 (1918).

‡ Note that $\boldsymbol{a}$ has been substituted for a, which is the surface excess actually measured and usually differs inappreciably from $\boldsymbol{a}$.

§ See, for example, Jeans, ‘Dynamical Theory of Gases.’

where V_a is the molecular volume of the adsorbate. This equation cannot be applied to the case of a liquid and its vapour, which is presumably due to the fact that the expression should really be written as

$$E = RT \log N_\alpha / N$$

where N_a and N are the number of impacts per second per unit area by the molecules in the two phases. N is not proportional to the concentration $1/V$ unless V is great. If the adsorption volume is of thickness δ comparable with σ the diameter of the molecule of the adsorbate, then the centre of the molecule oscillating in a thin lamina only moves through a distance $\delta - \sigma$ normal to the surface and not δ. Hence if S is the area of the adsorbent we see that N_α is proportional to $\alpha/S(\delta-\sigma)$ and not $\alpha/S\delta$, and hence we write our second equation as

$$E = RT \log \frac{V\alpha}{S(\delta-\sigma)} = RT \log \frac{\alpha}{w \,.\, c}, \tag{2}$$

where $w = S(\delta - \sigma)$.

The third expression is derived from the ordinary theory of attraction. Suppose the law of attraction of the adsorbent for the gas is given by the expression

$$-\partial E/\partial r = -\mu a^{\frac{1}{2}} a_0^{\frac{1}{2}} \phi'(r)$$

where μ is a universal constant and $a^{\frac{1}{2}}$ and $a_0^{\frac{1}{2}}$ are specific factors of attraction* for the gas and adsorbent respectively, and r is the distance measured from some point in the adsorbent to the centre of attraction of the molecule of the gas. Then if r_0 is the mean value of r for an adsorbed molecule, there being no change in the mean *kinetic* energy,

$$\begin{aligned} E &= \int_\infty^{r_0} \mu a^{\frac{1}{2}} a_0^{\frac{1}{2}} \phi'(r)\, dr \\ &= \mu a^{\frac{1}{2}} a_0^{\frac{1}{2}} \{\phi(r_0) - \phi(\infty)\} \\ &= \mu a^{\frac{1}{2}} a_0^{\frac{1}{2}} \phi(r_0). \end{aligned} \tag{3}$$

We may equate any two of the expressions obtained above. Thus from (1) and (2) we have

$$RT^2 \left(\frac{\partial \log c}{\partial T}\right)_\alpha = RT \log \frac{\alpha}{c \,.\, w};$$

whence

$$\frac{T\partial \log \alpha/c}{\partial T} + \log \frac{\alpha}{c} = \log w,$$

$$\frac{\partial T \log \alpha/c}{\partial T} = \log w,$$

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* Since the factor is proportional to the square root of the cohesion, we write $a^{\frac{1}{2}}$. (See Part III of this research.)

and therefore

$$\mathrm{T}\log \alpha/c = \text{constant} + \int^{\mathrm{T}} \log w d\mathrm{T}$$

$$= \text{constant} + \mathrm{T}\log w - \int^{\mathrm{T}} \frac{\mathrm{T}}{w} \cdot \left(\frac{\partial w}{\partial \mathrm{T}}\right)_{\alpha} d\mathrm{T}. \tag{4}$$

where the constant is some function of α but is independent of T. Again from (2) and (3) we have

$$\mathrm{T}\log \alpha/c = \mathrm{T}\log w + \mu/\mathrm{R} \,.\, a^{\frac{1}{2}} a_0^{\frac{1}{2}} \phi(r_0). \tag{5}$$

It is evident from these equations that if we assume w to be independent of the temperature, then $\mu\, a^{\frac{1}{2}}\, a_0^{\frac{1}{2}}\, \phi(r_0)$ is also independent of T, and we may write

$$\mathrm{T}\log \alpha/c = \mathrm{A} + \mathrm{BT}, \tag{6}$$

where A and B are independent of the temperature but are functions of α. For convenience of calculation it is better to write the above expression in the form

$$\log \alpha/c = \mathrm{B} + \mathrm{A}/\mathrm{T}. \tag{7}$$

This is evidently the equation for the *adsorption isosteres*—lines of constant α

Even if B and A are not independent of T if we expand the right-hand side of (7) in powers of α we get

$$\log \alpha/c = \mathrm{B}(o) + \left(\frac{\partial \mathrm{B}}{\partial \alpha}\right)_{\alpha = 0} \alpha +$$

$$+ \frac{\mathrm{A}(o)}{\mathrm{T}} + \frac{1}{\mathrm{T}} \cdot \left(\frac{\partial \mathrm{A}}{\partial \alpha}\right)_{\alpha = 0} \alpha +$$

$$= \mathrm{A}_0 - \mathrm{A}_1 \alpha, \tag{8}$$

neglecting powers of α beyond the first for moderate adsorptions. This new expression (8) is evidently the equation for the *adsorption isotherm*—the relation between α and c (or p) at constant temperature.

It is now necessary to examine to what extent equations (7) and (8) represent the results of observation, and thus to find how far the assumptions made in the simple theory are justified by experiment. For this purpose we will look at some adsorption isosteres and isotherms, and find (i) how far A and B are independent of temperature; (ii) to what extent powers of α beyond the first may be neglected in (8).

Part II.

(a) *The Adsorption Isosteres.*

It is as a rule difficult to obtain observations of an adsorption isostere over a very wide stretch of temperature. At high temperatures the adsorption is small save for very great pressures, while at low temperatures the adsorption is great even for small pressures. The examples here cited have been chosen as covering as wide a stretch of temperature as possible and providing a fair representation of the observations available.

Table I.

Argon (Homfray*) $\alpha = 1 \cdot 67$. $\log p/T = 1 \cdot 520 - 807/T$.
Crit. temp. $= -117°$ C. $\alpha_\infty = 110$.

p.	T	p calc.
cm.		
5	251·0	5·1
10	272·7	10·0
15	286·8	14·6
20	298·0	19·5
25	308·6	25·1
30	316·6	29·9
40	330·8	40·1
50	342·5	50·2
60	352·4	60·1

In Table I, T has been interpolated by Miss Homfray from observations at different temperatures. The method of interpolation is not that suggested by the equations (7) and (8) above, and hence there is introduced a small unknown error. Wherever possible the author has evaluated by extrapolation† from observations at low temperatures the saturation adsorption which is denoted by α_∞ in the Tables.

Table II.

Methane (Homfray) $\alpha = 7 \cdot 18$. $\log p/T = 2 \cdot 225 - 1050/T$.
Crit. temp. $-96°$ C. ($\alpha_\infty = 98$).

T.	p.	p calc.
	cm.	
240	1·7	1·7
255	3·4	3·3
273	6·6	6·6
293	12·8	13·0
319	28·9	27·7
351	61·2	60·8
373	(96·2)	97·0
455	(392)	380

In Table II the values of p in the second column have been interpolated from observations at constant temperature. The values in brackets are extrapolated. Fig. 1 presents in graphical form the results of other interpolations by the author. The rectilinear form of the $(1/T, \log p/T)$ curves is obvious.

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* 'Zeits. f. Physikal. Chem.,' vol. 74, p. 129 (1910).

† 'Trans. Farad. Soc.,' vol. 10, p. 167 (1914).

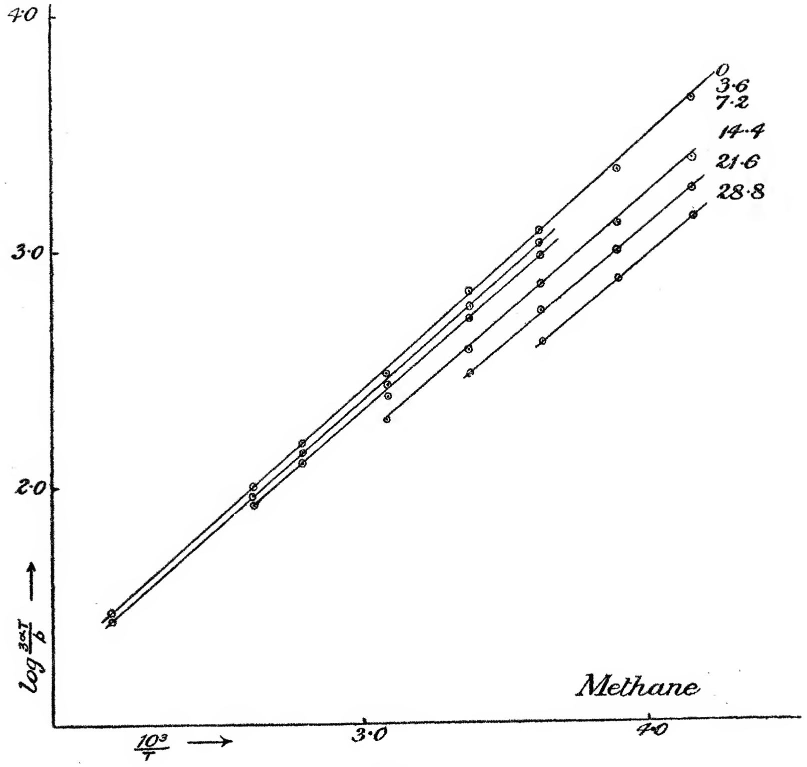

Fig. 1.

Table III.

Carbon dioxide (Chappuis*) $\alpha = 282$. $\log p/T = 4{\cdot}269 - 1398/T$.
Crit. temp. 31° C. (α_∞ circa 2000).

T.	p (Chappuis).	p.	p calc.
273 ·0	3 ·8	3 ·8	3 ·8
286 ·0	7 ·5	7·0	6 ·9
290 ·5	8 ·7	8 ·4	8 ·3
298 ·7	12 ·5	11 ·7	11 ·6
304 ·7	15 ·8	14 ·7	14 ·7
308 ·7	18 ·7	17 ·2	17 ·0
320 ·0	27 ·6	25 ·6	25 ·4
323 ·7	31 ·1	28 ·8	28 ·8
329 ·6	37 ·8	35 ·5	35 ·2
332 ·3	40 ·7	38 ·8	38 ·4
338 ·5	48 ·7	46 ·8	46 ·7
348 ·0	62 ·8	62 ·2	62 ·2
349 ·1	64 ·6	63 ·8	64 ·1
355 ·8	77 ·1	77 ·1	77 ·8

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* 'Wied. Ann.,' vol. 12, p. 161 (1881).

In Table III the values headed "p (Chappuis)" have been interpolated by Chappuis on the erroneous assumption that "the increase of adsorption with pressure at any temperature between 0° C. and 83° C. is proportional to that at 0° C." The column headed "p" has been interpolated by the author from Chappuis's observations by plotting on the same sheet the $(\alpha, \log \alpha T/p)$ points for *all* his observed values at different temperatures and then extrapolating to $\alpha = 282$, using the fact that the points for a given temperature lie on a straight line which does not intersect the lines for other temperatures. This extrapolation, though laborious, is very easy. The values of α in this case refer to 15 c.c. of charcoal—say 27 grm. In all other cases the values are referred to 1 grm. of that adsorbent, the only one here considered.

Table IV.

Ammonia (Richardson*) $\alpha = 15$. $\log p/T = 3{\cdot}193 - 1628/T$.
Crit. temp. 130° C. $\alpha_{\infty} = 154$.

T.	p.	p calc.
	cm.	
273	0·6	0·5
283	0·9	0·8
293	1·3	1·3
303	2·0	2·0
313	3·0	3·1
328	5·5	5·5
343	9·6	9·6
358	16·1	15·8
373	25·6	25·1
388	37·9	38·5
403	56·5	57·3
418	83·4	83·0
433	116	117
448	158	162
473	268	267

The observations on ammonia considered in Table IV are interesting inasmuch as most have been made at temperatures *below* the critical point. The deviations at the lowest temperatures, though small, are apparently systematic and are emphasised in the isosteres for greater values of α, which are presented in graphical form in fig. 2.

The special case of the isostere of zero adsorption is considered in Part III where many examples are discussed in connection with the theoretical aspect of the constants A and B of the formula.

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* 'Jour. Amer. Chem. Soc.,' vol. 39, p. 1828 (1917).

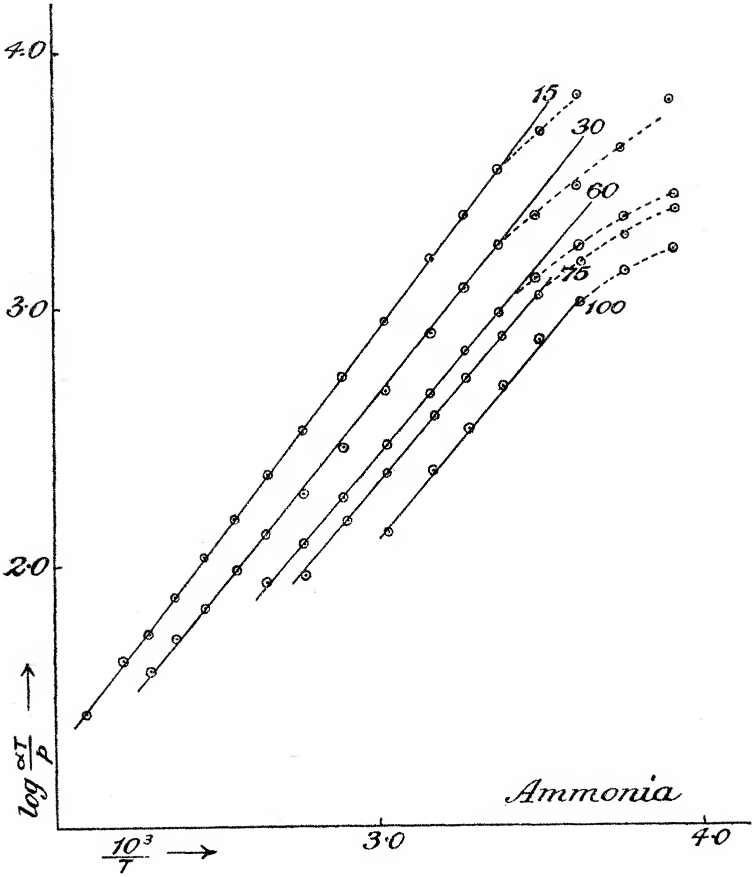

FIG. 2.

(b) *The Adsorption Isotherms.*

As examples of the applicability of the formula (8) the cases below are selected from a mass of data and calculations. For comparison there are also given the values calculated from the best values of the constants in the well-known "exponential" formula

$$\alpha = \alpha_0' c^{1/n}$$

in the form $$\log \alpha = \log \alpha_0' + 1/n \log c.$$

Table V.

Nitrogen at 0° C. (Titoff*) $\log \alpha/p = \bar{1}{\cdot}415 - 0{\cdot}0143\,\alpha$ (I).
Crit. temp. −146° C. $\alpha_\infty = 96$. $\log \alpha = \bar{1}{\cdot}424 + 0{\cdot}927 \log p$ (II).

p.	α Obs.	α Calc. (I).	α Calc. (II).
cm.	c.c.		
0·43	0·111	0·111	0·123
1·21	0·298	0·312	0·318
3·93	0·987	0·990	0·938
12·98	3·04	3·06	2·87
22·94	5·08	5·06	4·81
34·01	7·05	7·02	7·02
56·23	10·31	10·37	11·12
77·46	13·05	13·09	14·86

Table VI.

Methane at 0° C. (Homfray, *loc. cit.*) $\log \alpha/p = 0{\cdot}166 - 0{\cdot}0165\,\alpha$ (I).
Crit. temp. −95° C. ($\alpha_\infty = 98$). $\log \alpha = 0{\cdot}497 + 0{\cdot}545 \log p$ (II).

p.	α Obs.	α Calc. (I).	α Calc. (II).
cm.	c.c.		
6·7	7·4	7·4	9·1
13·4	12·3	12·3	12·8
19·1	15·9	15·5	15·7
27·4	19·1	19·3	19·0
35·8	22·3	22·4	22·0
45·1	25·3	25·2	25·0
57·8	28·4	28·6	28·8
70·2	31·3	31·3	32·0

Table VII.

Carbon monoxide at −82° C. (Homfray). $\log \alpha/p = 1{\cdot}132 - 0{\cdot}0219\,\alpha$ (I).
Crit. temp. −41° C. ($\alpha_\infty = 94$). $\log \alpha = 1{\cdot}062 + 0{\cdot}400 \log p$ (II).

p.	α Obs.	α Calc. (I).	α Calc. (II).
cm.			
0·6	6·2	6·2	9·4
3·0	17·1	17·1	17·9
4·0	19·4	19·9	20·1
7·2	25·7	26·1	25·4
7·5	26·2	26·6	25·8
11·7	31·7	31·3	30·8
14·8	34·7	34·7	33·9
18·7	37·6	37·6	37·2
28·8	43·3	43·4	44·3
42·2	49·3	48·8	51·5

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* 'Zeits. f. Physikal. Chem.,' vol. 74, p. 641 (1910).

The close agreement of the theoretical formula with experiment is shown by the very numerous observations of Chappuis[*] contained in Table VIII. These are probably the most accurate existing data at any one temperature. They illustrate also the systematic increasing deviation between the calculated and observed values when the adsorption becomes great. The divergence otherwise appears to be within the limits of error of observation of the pressure and is nowhere large, save initially, and here an error of only 0·023 cm. would cover the deviation, since the calculated value of p for $\alpha = 10{\cdot}45$ is 0·090.

Table VIII.

Carbon dioxide at 0° (Chappuis). $\log \alpha/p = 2{\cdot}0727 - 0{\cdot}000720\,\alpha$.
Crit. temp. 31° C. (α_∞ circa 2000).

p.	α Obs.	α Calc.	Per cent. div.
cm.	c.c.		
0·113	10·45	13·0	+24·0
0·223	23·18	25·2	+ 9·0
0·305	34·0	33·9	− 0·3
0·470	52·7	50·9	− 3·4
0·580	61·5	61·7	+ 0·3
0·670	71·9	70·3	− 2·2
0·780	81·8	80·2	− 2·0
0·905	91·2	91·6	+ 0·4
0·986	100·6	98·6	− 2·0
1·100	110·1	108·2	− 1·7
1·240	119·9	119·8	− 0·1
1·352	129·5	128·6	− 0·7
1·495	139·6	139·7	+ 0·1
1·625	149·3	149·4	+ 0·1
1·762	158·9	159·3	+ 0·3
1·882	168·4	167·9	− 0·3
2·012	178·2	176·8	− 0·8
2·170	188·1	187·4	− 0·4
2·312	198·1	196·5	− 0·8
2·494	208·4	207·9	− 0·2
2·641	218·3	217·0	− 0·6
2·822	228·3	227·8	− 0·2
2·998	238·2	238·0	− 0·1
3·175	248·1	247·9	− 0·1
3·392	258·3	259·8	+ 0·6
3·548	268·2	268·1	− 0·0
3·755	278·5	278·6	+ 0·0
3·975	289·6	289·8	+ 0·1
4·194	300·5	300·5	± 0·0
4·427	311·1	311·4	+ 0·1
4·693	324·4	323·5	− 0·3
5·078	341·2	340·2	− 0·3
5·463	357·8	356·7	− 0·3
5·984	377·5	377·5	± 0·0
6·413	393·2	393·8	+ 0·2
6·567	398·8	399·5	+ 0·2
7·010	414·2	415·4	+ 0·3
7·712	438·2	439·3	+ 0·3

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[*] *Loc cit.*

Table VIII—*continued.*

p.	α Obs.	α Calc.	Per cent. div.
cm.			
8·548	464·6	465·9	+ 0·3
9·437	491·8	492·3	+ 0·1
10·41	519·4	519·2	− 0·0
11·51	547·6	547·8	+ 0·0
12·63	575·8	574·9	− 0·2
13·80	602·8	601·5	− 0·2
15·14	630·8	629·6	− 0·2
16·58	659·2	658·2	− 0·2
18·05	686·4	685·3	− 0·2
19·67	714·2	713·2	− 0·1
21·57	744·0	743·3	− 0·1
23·67	774·5	774·8	+ 0·0
25·81	804·2	804·6	+ 0·0
28·17	833·7	835·0	+ 0·2
30·84	863·4	867·0	+ 0·4
33·50	892·8	896·8	+ 0·4
36·47	921·6	927·8	+ 0·7
39·68	950·6	958·8	+ 0·9
43·05	978·2	989·3	+ 1·1
46·49	1006	1019	+ 1·3
50·36	1033	1049	+ 1·6
54·31	1059	1077	+ 1·7
59·20	1087	1112	+ 2·3
64·64	1114	1147	+ 3·0
70·34	1140	1182	+ 3·7
76·34	1166	1216	+ 4·3

In view of the use that the author has made of the equation (8) in extrapolating to the value of $\log \alpha/c$ at zero concentration, discussed at length in Part III, it is of interest to examine the complete $(\alpha, \log \alpha/c)$ curve. This is presented in fig. 3, which is based upon the author's observations[*] on sulphur dioxide at −10° C., that is, 165° C. below its critical point. It will be seen that there are three portions—A to B, B to C, C to D—any one of which might be approximately represented by a straight line. In the case of gases *below* their critical temperature the portion AB becomes very steep, and extrapolation to A is difficult. This is shown by ammonia in the case of the observations of Titoff and of Richardson even *above* the critical temperature, and hence in these cases the equation (8) cannot be used for extrapolation. In the other cases examined, mainly gases *above* their critical temperature, the portion A to C is very nearly rectilineal, and extrapolation is consequently justifiable for observations up to 30 per cent. of the saturation adsorption, and is exemplified in the case of ethylene in fig. 4, in Part III.

[*] ‘Proc. Roy. Soc. Edin.,’ vol. 37, p. 161 (1917).

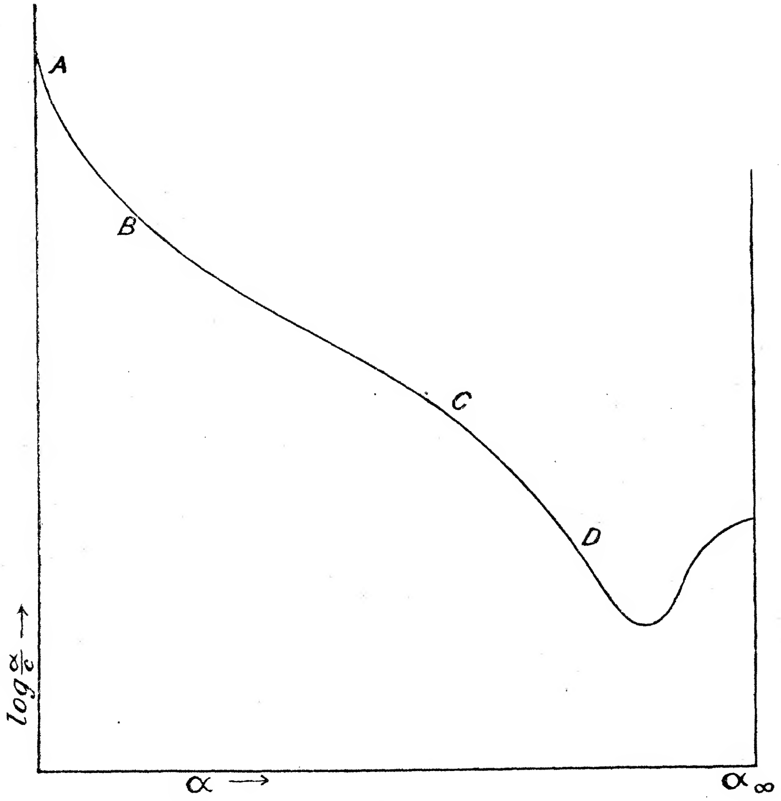

FIG. 3.

Summary of Parts I and II.

1. The theoretical form of the adsorption isostere is deduced and found to be

$$\log \alpha/c = B + A/T$$

where B and A are functions of α only.

2. The agreement with observation for gases above or near the critical temperature is satisfactory.

3. The theoretical form of the adsorption isotherm is deduced and found to be

$$\log \alpha/c = A_0 - A_1\alpha$$

where A_0 and A_1 are functions of the temperature only.

4. The agreement with observation up to moderate adsorptions of gases above their critical temperature is satisfactory.

The author wishes to thank Prof. James Walker, F.R.S., for his valuable assistance in the presentation of this paper.